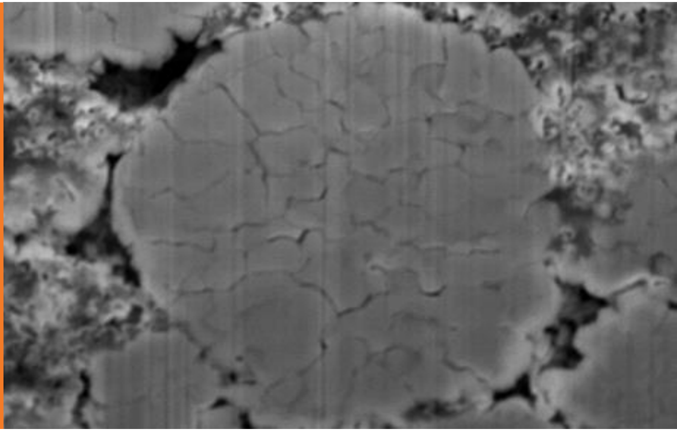
eXtreme Fast Charge Cell Evaluation
of Lithium-ion Batteries

BAT340: IMPACTS OF CHARGING ON CELL DEGRADATION



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U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy
VEHICLE TECHNOLOGIES OFFICE

June 12, 2019
Arlington, VA

OVERVIEW

Timeline

- Start: October 1, 2017
- End: September 30, 2021
- Percent Complete: 37%

Barriers

- Cell degradation during fast charge
- Low energy density and high cost of fast charge cells

Budget

- Funding for FY19 – 6390k
  - ANL – 2400k
  - NREL – 1600K
  - INL – 440K
  - SLAC – 1000K
  - LBNL – 950K

Partners

- Argonne National Laboratory
- Idaho National Laboratory
- Lawrence Berkeley National Lab
- National Renewable Energy Laboratory
- SLAC National Accelerator Lab

XCEL
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RELEVANCE

Impact:

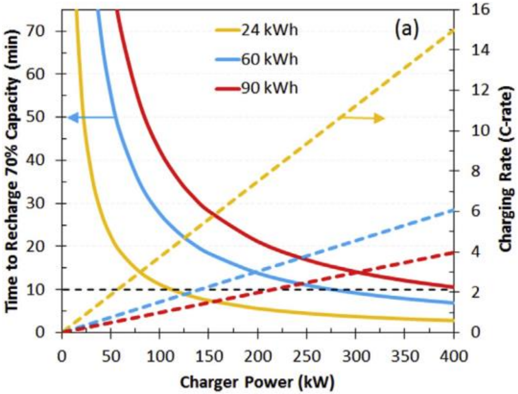
Increase electric vehicle adoption by decreasing charge time

Mitigate cycle life issues due to Li plating and heat when charging above 4C

Refine key challenges in identifying Li plating, materials degradation, electrode design and transport.

Objective

Using full cells to identify and quantify failure modes, provide insight into materials degradation after cycling and areas where materials/electrolyte advance can be made.



Ahmed et. al, J. Power Sources, 367 (2017), 250

MILESTONES

INL related milestones in XCEL

Milestone	End Date	Status
Quantitate Single Layer Pouch Cell Failure Modes	12/31/2018	Complete
Identification of enhanced transportation electrolytes	3/31/2019	Complete (also see Bat371)
Characterization of electrochemical Li reversibility	6/30/2019	In progress
Correlate electrochemical and acoustic signals	9/30/2019	In progress

APPROACH

Impacts of high rate charging

- Identify charge acceptance limitations
- Understand overvoltage due to transport, charge transfer and ohmic contributions
- Evaluate changes as a function of aging

Identify key barriers as different charge conditions are used

- Focus on clearly identifying limitations and benefits

Identify electrochemical signals for reversible Li plating

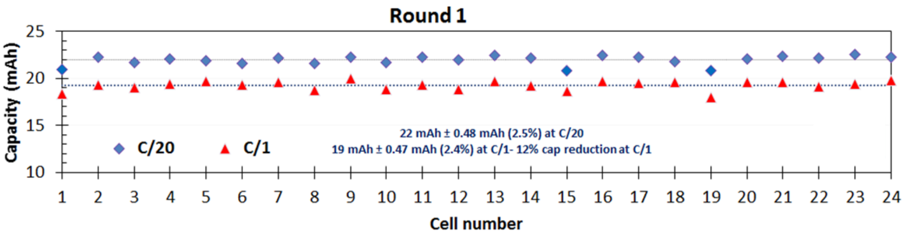
Provide assorted samples to other team members after completion of evaluation

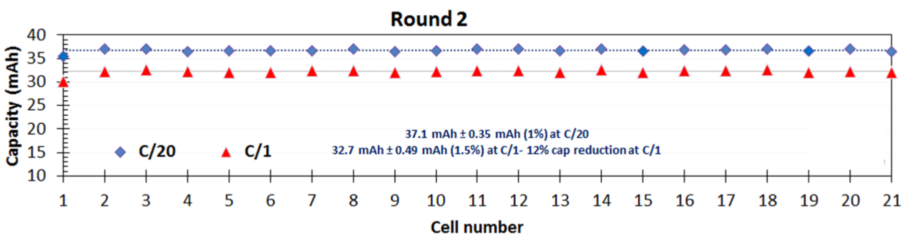
EVALUATION AND PROTOCOL DEVELOPMENT

LOW VARIABILITY FOR AS RECEIVED CELLS

Test set up and design

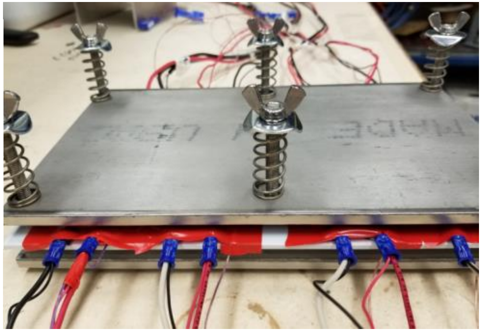
- Low variability as received
  - Round 1 – 1.9 mAh/cm^2
  - Round 2 – 3.0 mAh/cm^2





Lexan spacer

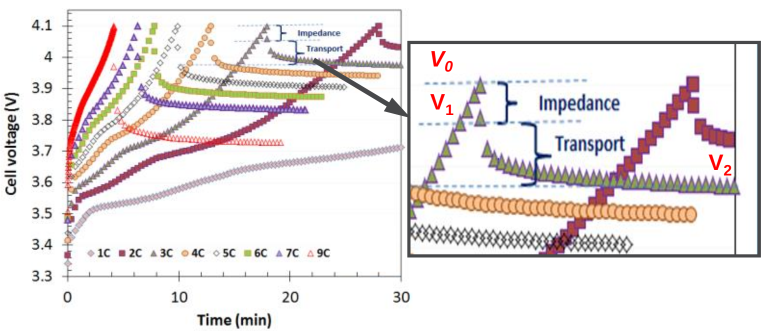
Polypropylene

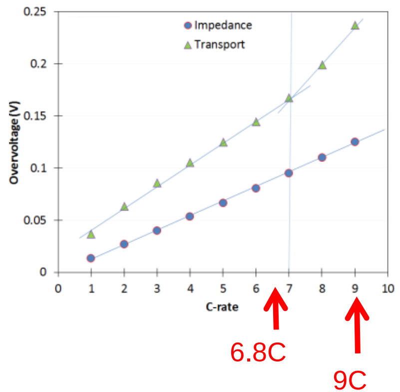


PROTOCOL DEVELOPMENT

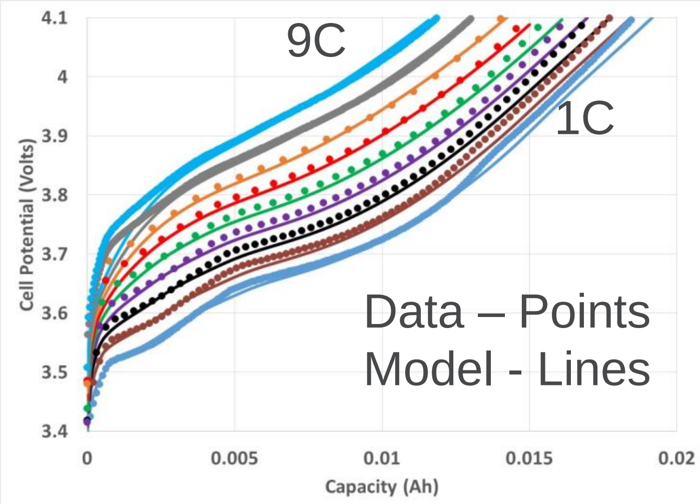
Transport Characterization – Round 1 (1.9 mAh/cm^2)

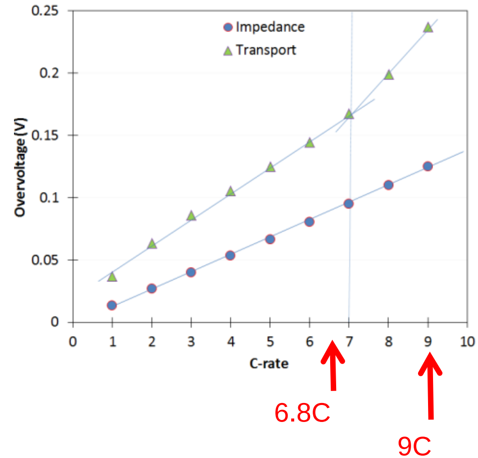
- Overvoltage due to impedance (immediate relaxation- *ms*) and transport (extended relaxation-15 min)
- Impedance (ohmic+ Rxn polarizations) varies linearly w/ C-rate
- **Distinct transport limitation arises above 7C**

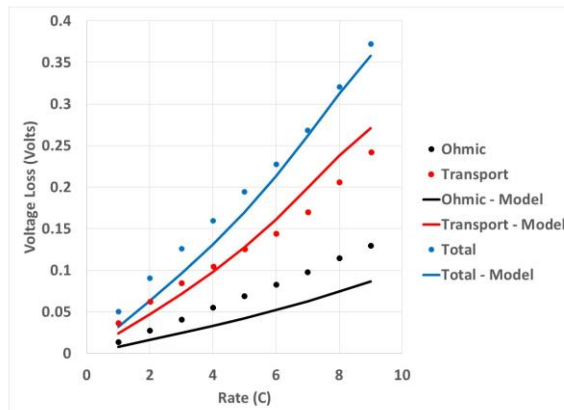




ALIGNMENT WITH MODELING







- Electrodes ~40 microns thick, ~35% porosity (1.5 mAh/cm^2)
- Linear overpotential with rate
- See ES371

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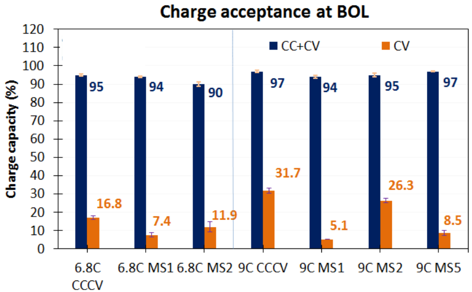
PROTOCOL DEVELOPMENT

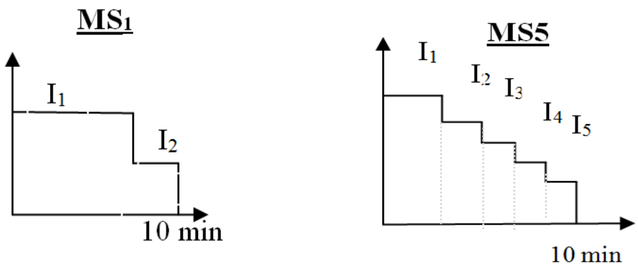
Protocols to minimize transport limitations

- Multiple ways to achieve 95+% charge acceptance in 10 min
- Multi-step profiles reduce time in CV
  - Less time at maximum voltage

Gr.	Cell count	10 min charging protocol
B	4 to 6	6.8C CCCV
C	8 to 10	6.8C MS1 (2-step current)
D	11 to 13	6.8C MS2 (pulsed current)
E	14, 16 and 17	9C CCCV
F	18, 20, and 21	9C MS1 (2 step current)
G	22 to 24	9C MS2 (pulsed current)
H	15 and 19	9C MS5 (5 step current)



Total charge time 10 min



Step determined by beginning of life overvoltage and maintaining a 10 min charge

AGING

Benefits from profile in reducing aging

- High variability for most charge profiles
- Multi-step profiles have slightly reduced variability

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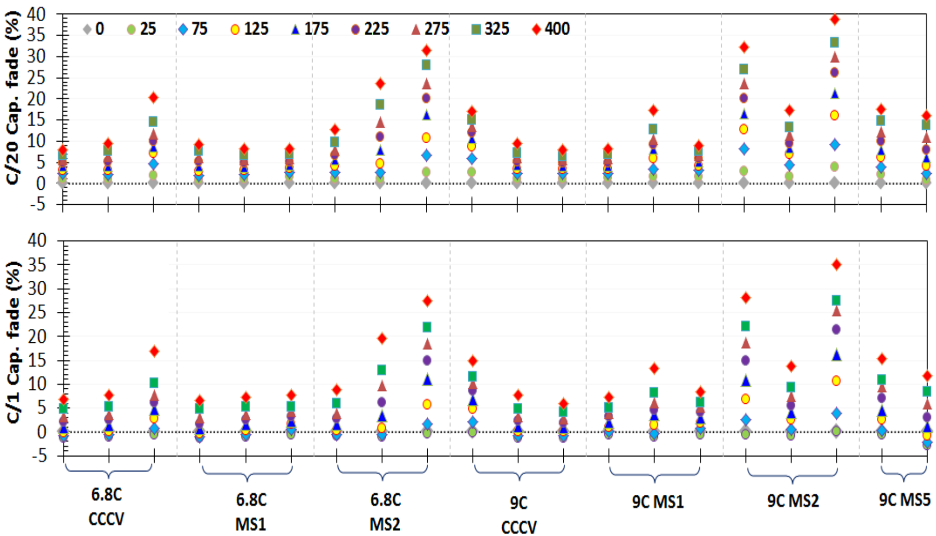
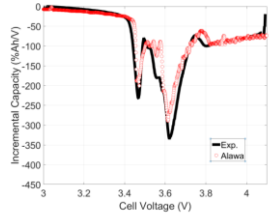


CHARACTERIZATION AND FAILURE ANALYSIS – ROUND 1

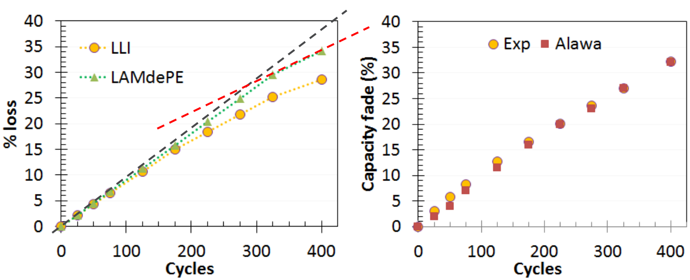
UNDERSTANDING FAILURE

Multiple degradation modes

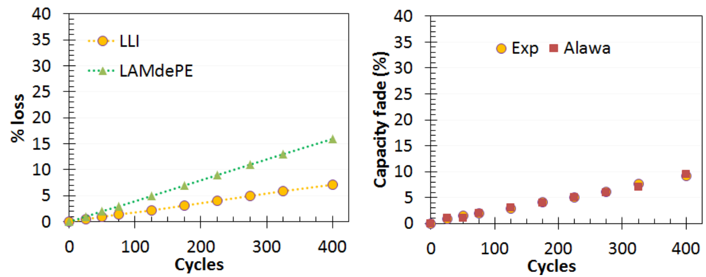
- Experimental dQ/dV compared to simulated fade using Alawa
- Best fit aligned combined loss of Li inventory (LLI) and loss of cathode material (LAM_{dePE}) - for highest fade some change in rate near end of testing
- Rates of fade vary as does ratio of LLI:LAM_{dePE}



33% fade



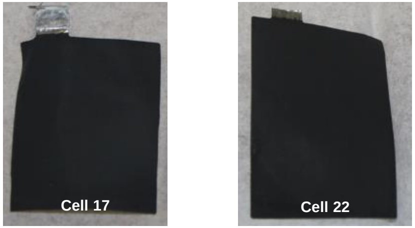
8% fade

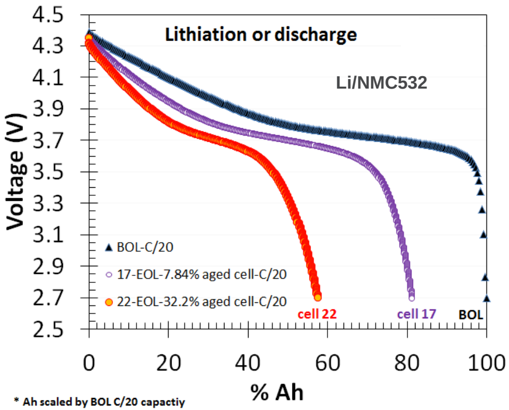


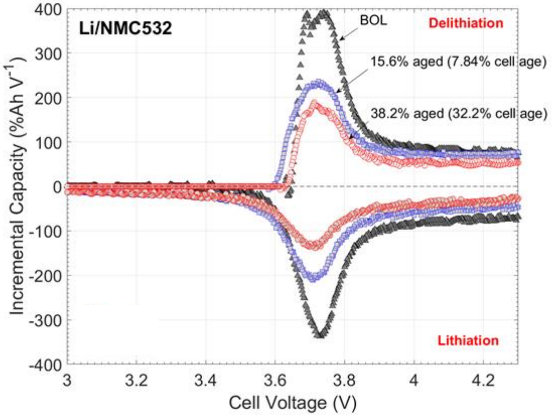
SIGNIFICANT CATHODE FADE

Verification of cathode fade

- Post-test extraction of cathodes indicates no delamination
- Cycling in a half cell at C/20 shows significant fade
- dQ/dV suggests both active material loss and suppressed kinetics



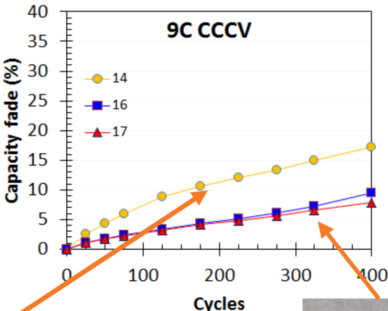


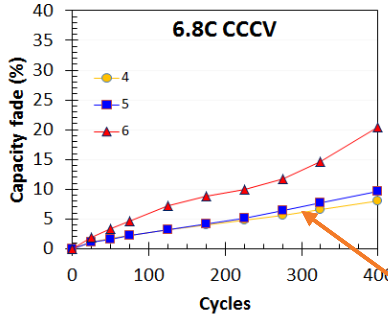


OTHER FAILURE MODES

Li Plating?

- Most cells show few signs of Li plating
- Not all cells in a charge condition had visual signs of plating
- Li that was observed only in isolated locations



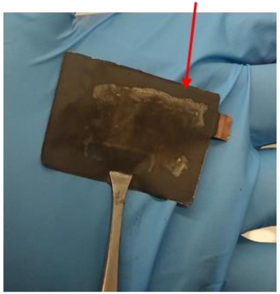


POST-TEST CHARACTERIZATION

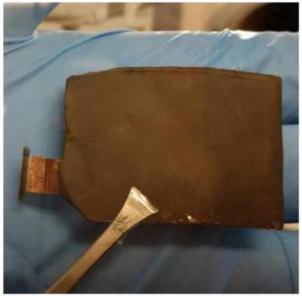
Tested at INL, then sent to ANL for additional characterization

Lithium deposit
Greyish areas

9-C MS2



9-C CC/CV

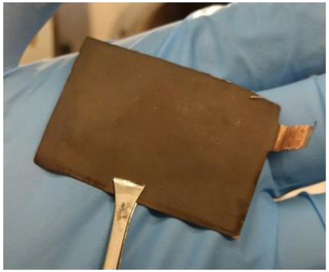


9-C MS5

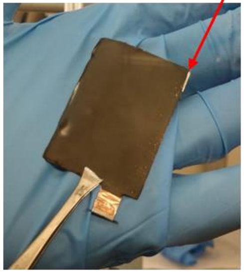
Missing coating

6.8-C MS1

9-C MS1



6.8-C MS2



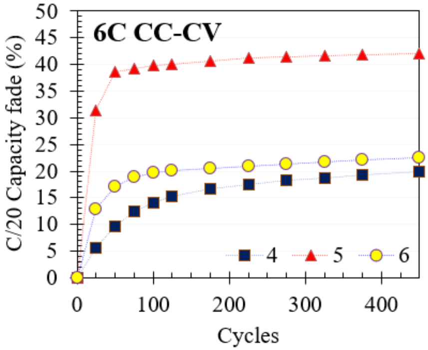
6.8-C CC/CV

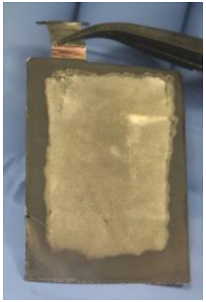
CHARACTERIZATION AND FAILURE ANALYSIS – ROUND 2

CYCLING PERFORMANCE AT HIGHER LOADING

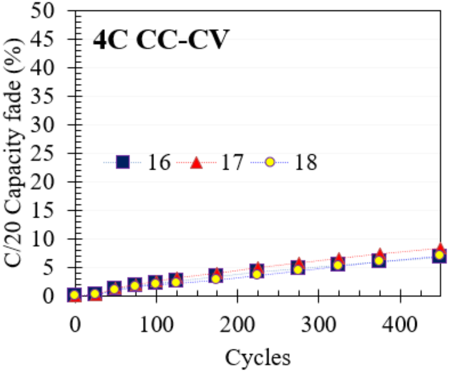
Round 2 (3.0 mAh/cm^2 loading)

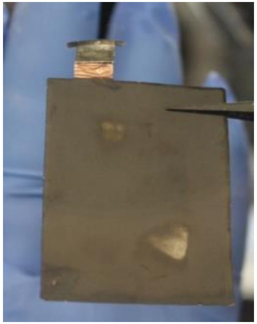
- Higher loading, more pronounced transport limitations
- More direct visual observation of Li – Aligns with XRD from SLAC
- Lower loss of cathode active material at low rates
- Variability still prominent





Cell 5





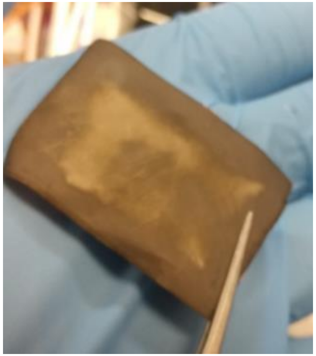
Cell 16

IMPACT OF TEMPERATURE IN POUCH CELLS

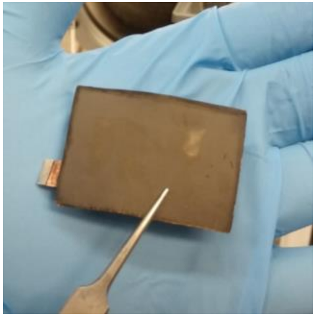
Following Cell Testing at Argonne's EADL at Select Temperatures

- Lithium plating observed during post-test analysis
- Extent of plating seems to inversely depend on test temperature (expected)

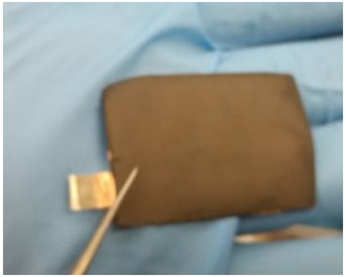
20°C



30°C



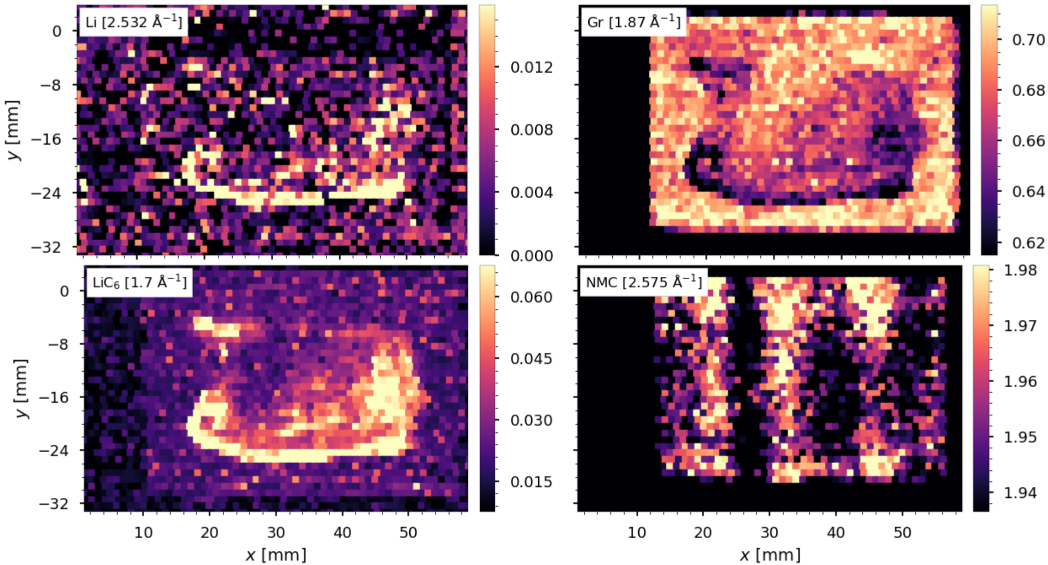
40°C



50°C

IN SITU VERIFICATION OF PLATING LI

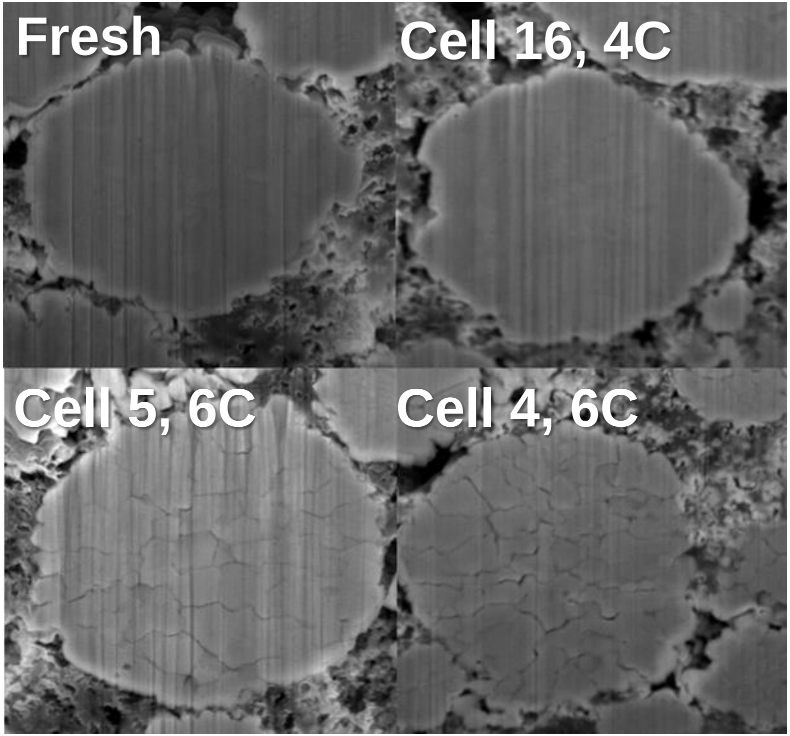
Cycling: 6C, CCCV, 450 cycles

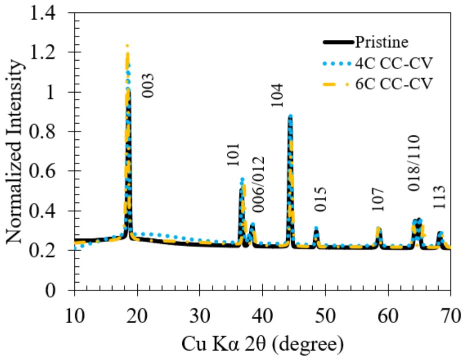


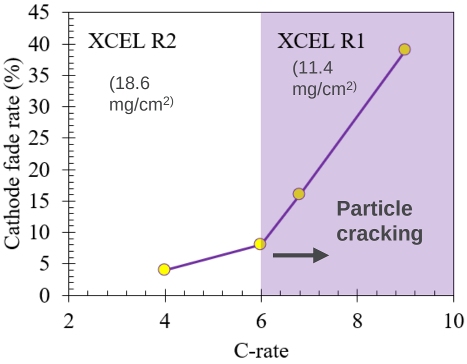
- Intensities of Li and Gr anti-correlated
- Intensities of Li and LiC_6/LiC_{12} correlated
- NMC shows pattern; no obvious correlation with Li
- See ES 384

ADDITIONAL CATHODE FADE

Cathode cracking at high rates, but no apparent bulk cation mixing







RESPONSE TO PREVIOUS YEARS REVIEWERS' COMMENTS

Not previously reviewed

COLLABORATION ACROSS LABS AND UNIVERSITIES

Argonne National Laboratory: Cell and electrode design and building, performance characterization, post-test, cell and atomistic modeling, cost modeling

Berkeley Lab: Li detection, electrode architecture, diagnostics

INL: Performance characterization, Li detection, failure analysis, electrolyte modeling and characterization, acoustic detection (with Princeton)

NREL: Thermal characterization, life modeling, micro and macro scale modeling, electrolyte modeling and characterization

SLAC: Li detection, novel separators, diagnostics

REMAINING CHALLENGES AND BARRIERS

- Refine analysis on cathode fade and mechanical fracturing
- Refine understanding of electrolyte transport
- Cross-correlate Li detection across organizations using different methods

PROPOSED FUTURE RESEARCH

- Expand fundamental understanding of cathode cracking associated with high rate charging
  - Electrolyte impacts
  - Expanded design-of-experiments to capture emergence of cracking
  - Rate and protocol drivers for cracking
- Cell variability analysis
  - Understand how electrode structures and localized variation drive degradation (both cathode and anode)
  - Localized Li plating – identify drivers, emergence and growth mechanisms
- Continue to identify and ameliorate transport limitations
  - Extended performance analysis – Do the electrolytes also enable high cycle life
  - Li plating and cathode cracking implications

Any proposed future work is subject to change based on funding levels

SUMMARY

- Elevated rates enhance cathode cracking
  - Fade associated with loss of cathode material close to observed losses of Li inventory
- Distinct locations of Li observed after testing
  - Direct electrochemical detection of Li during cycling difficult
  - Only at most elevated fade conditions is broad plating of Li observed
- Rates up to 4C appear to be reasonable
  - Transport still a key limitation that needs to be addressed
  - Less than 10% fade over 450 fast charge cycles

CONTRIBUTORS AND ACKNOWLEDGEMENTS

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SLAC NATIONAL ACCELERATOR LABORATORY

NREL NATIONAL RENEWABLE ENERGY LABORATORY

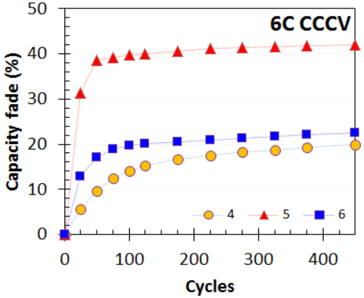
BERKELEY LAB Lawrence Berkeley National Laboratory

INL Idaho National Laboratory

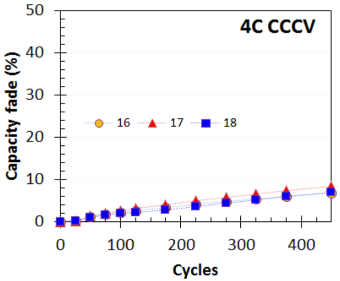
TECHNICAL BACKUP SLIDES

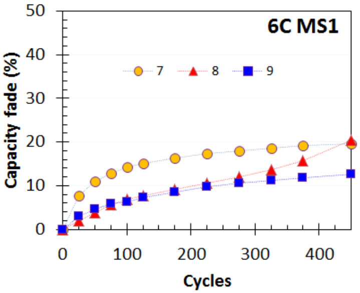
Additional Round 2 Aging

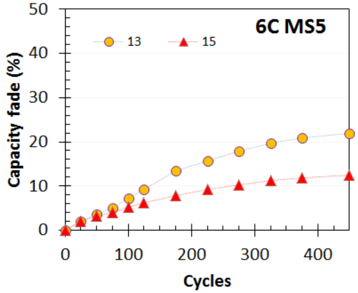
10 min (80% charge) protocol



15 min (90% charge) protocol



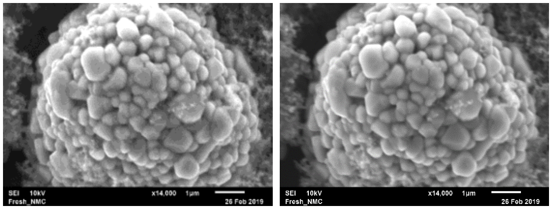




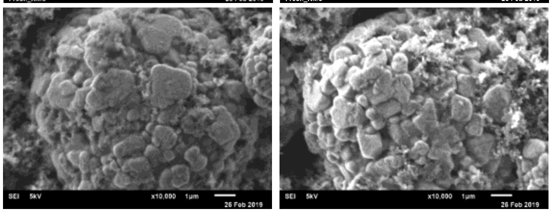
- Variability increased for 10 min profiles
- Fade rate distinctly different from Round 1
- 6C MS5 had initial rate of 7.5C

TECHNICAL BACKUP SLIDES

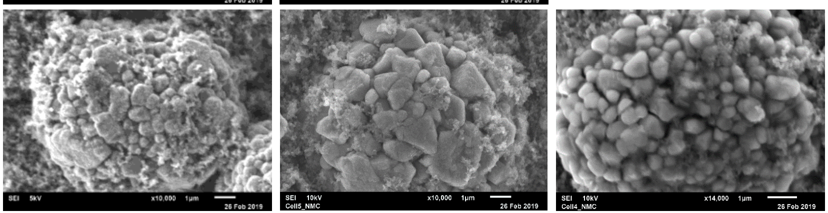
Cathode SEM – Round 2



Fresh Cathode Laminate



4C CC-CV (cell 16) after 450 cycles



6C CC-CV after 450 cycles

Non-FIB SEM does not clearly identify cracking

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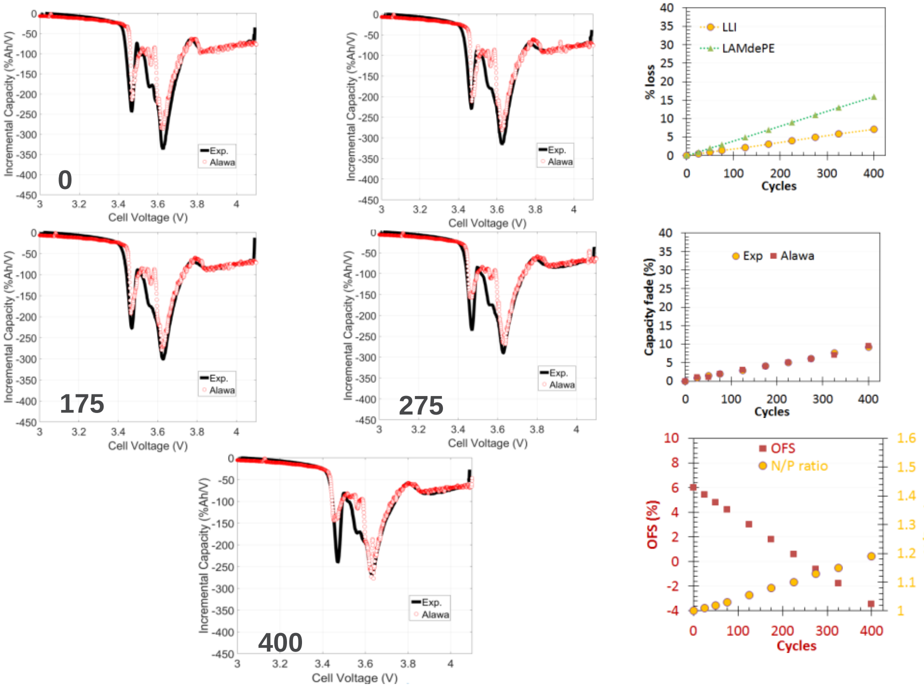
TECHNICAL BACKUP SLIDES

Example Alawa Analysis



Offset and N:P ratio distinctly shift with aging due to cathode loss